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Ship Materials Engineering Department
Research & Development Report**Influence of Expanding Monomer on Carbon Fiber
Reinforced Epoxy Composites**by
Barbara F. HowellInfluence of Expanding Monomer on Carbon Fiber
Reinforced Epoxy Composites

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ABSTRACT

In this investigation it was confirmed that copolymerization of dinorbornene spiroorthocarbonate (DNSOC) with epoxy can eliminate sample shrinkage and even produce sample expansion. To maximize control of shrinkage, it is important to bring epoxy to the gel stage before the DNSOC begins to copolymerize.

Embedded single filament tensile test results were compared for samples containing DGEBA-epoxy cured with m-phenylene diamine (mPDA) with those for DNSOC-epoxy samples cured with mPDA and BF_3 . diethylenetriamine for which BF_3 was used to catalyze polymerization of the DNSOC. As compared with epoxy, the DNSOC sample showed ten-fold reductions in interfacial tensile stress, 10°C reduction in T_g , and 40% reduction in tensile strength. The tensile modulus was not reduced and the sample showed no shrinkage. No stress patterns were seen in the DNSOC-epoxy with a polarizing microscope. It is concluded that smaller amounts of DNSOC than 12% can be used to produce optimal effects on mechanical properties.

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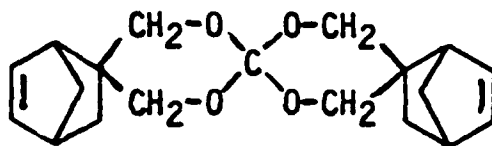
The author wishes to acknowledge the guidance and many helpful suggestions of Dr. William J. Bailey, University of Maryland. Assistance from Dr. M.R. Piggott, University of Toronto, and Dr. Murray Cohen, Epolin, Inc., is also acknowledged and is appreciated. Thanks are also due George Long and Timothy Dapp of DTRC.

INTRODUCTION

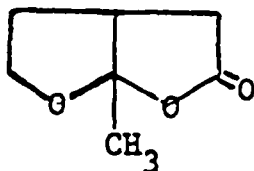
Carbon fiber reinforced composites have been found to be more susceptible to impact damage than are glass fiber reinforced composites, but the reason for this is not clearly understood. This work was undertaken to test the hypothesis proposed by Dr. Michael Piggott of the University of Toronto that the brittleness is caused by too great an interfacial pressure which is produced on the carbon fibers by shrinkage of the epoxy matrix. This excessive pressure is believed by Dr. Piggott to produce strains in the matrix, and he has demonstrated that inclusion of a material which reduces matrix shrinkage improves the mechanical properties of carbon fiber reinforced epoxies.

Materials which reduce polymer shrinkage were first prepared by Dr. William Bailey (1977) and coworkers at the University of Maryland. These monomeric materials contain two heterocyclic rings which open as the monomer polymerizes so that the polymer occupies a greater volume than that occupied by monomers of the unpolymerized material. This type of compound is known as an expanding monomer.

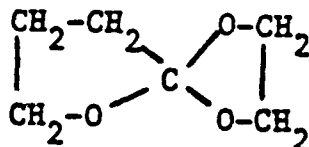
Spiroorthocarbonates are one type of expanding monomer, and of these dinorbornene spiroorthocarbonate (DNSOC) is used most frequently and is commercially available. DNSOC has the following structure.



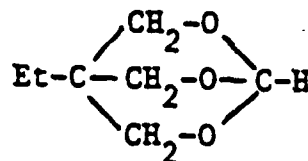
Other expanding monomers synthesized by Bailey (1977) and coworkers are ketal lactones, spiroorthoesters, and trioxabicyclooctanes. Structures for these compounds are shown below.



a ketal lactone

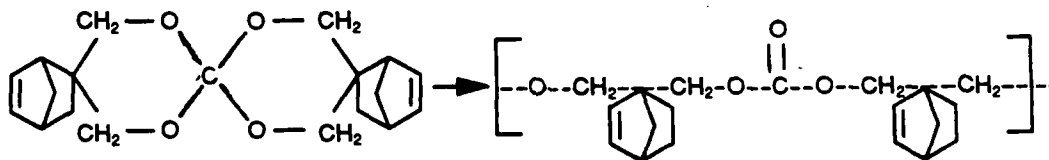


1,4,6-trioxaspiro[4.4]nonane, a spiroorthoester



2,6,7-trioxabicyclo[2.2.2]octane

Expansion occurs when an expanding monomer such as DNSOC polymerizes because distances separating atoms forming the heterocyclic ring are covalent bond distances. These distances are increased when the bonds break during polymerization as shown below.



Since, for small atoms, conversion of a covalent bond to the van der Waals distance (which separates atoms following the bond breaking) gives a threefold increase in separation, this effect greatly overshadows the bond shortening produced by the carbonyl double bond formation which also occurs as the bonds break (Bailey, 1977).

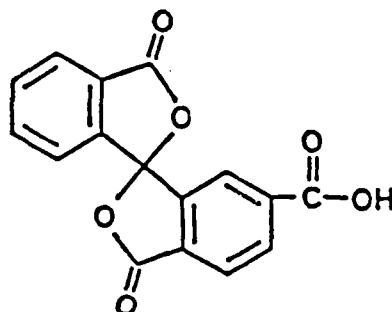
A second factor contributing to shrinkage reduction when expanding monomers are employed is the monomer change from solid to liquid which occurs as the polymerization takes place.

$$\text{CH}_2=\text{C} \begin{array}{c} \diagup \text{CH}_2-\text{O} \\ \diagdown \text{CH}_2-\text{O} \end{array} \text{C} \begin{array}{c} \diagup \text{O}-\text{CH}_2 \\ \diagdown \text{O}-\text{CH}_2 \end{array} \text{C}=\text{CH}_2$$

He has proposed that the matrix shrinkage stress should approximately equal the fiber Poisson shrinkage at the breaking point. Therefore, for glass fibers, 25-30 MPa is optimal, but for carbon fibers the pressure should be 10-15 MPa. However, for carbon fiber reinforced epoxies the shrinkage stress is approximately twice this value. Therefore, he proposes that addition of a substance which reduces epoxy shrinkage during curing will produce a more impact-resistant carbon fiber reinforced epoxy. Dr. Piggott and co-workers found that 7.5% DNSOC produced a carbon fiber epoxy with toughness increased by 100%.

Ishido and Nigro (1988) investigated the influence of DNSOC incorporation into epoxies. They employed dynamic mechanical spectroscopy and FTIR to monitor the curing of a system for which $\text{BF}_3 \cdot \text{MEA}$ (the boron trifluoride complex with monoethylamine) was the sole curing agent. For this system they found that only 8 to 10% of the DNSOC remained unreacted after the epoxy gel stage was reached. They conclude that for this system DNSOC alters resin thermal properties so that less cure shrinkage is converted into residual stress by lowering the T_g of the DNSOC-epoxy.

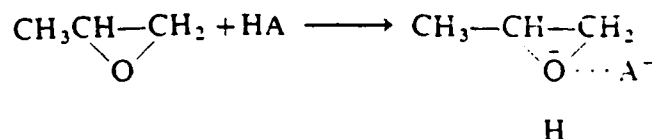
More recently, Dr. Allison Sikes, under the supervision of Dr. Robert Brady, of the Naval Research Laboratory has synthesized additional monomers which undergo expansion by an anionic polymerization mechanism (Sikes, 1989). These compounds contain spirobislactone groups which open during curing with epoxies. For this work epoxies were cured with acid anhydrides. The spirobislactone carboxylic acid



was used to end cap bisphenol A, tetramethylbenzene dimethanol, 1,4-bis(2-hydroxy-2-propyl) benzene, and hydroquinone. Each of these was copolymerized separately with DGEBA (diglycidylether of bisphenol A) epoxy by standard anhydride-epoxy polymerization procedures. Infrared spectroscopy and thermal analysis were used to monitor polymerization during curing. All three endapped monomers produced had greater thermal stability than the epoxy cured only with anhydride.

In addition, an aliphatic and an aromatic spirobislactone were synthesized and incorporated into epoxies. Cure was once again monitored by infrared and differential scanning calorimetry, and embedded single filament tensile tests were performed as were mechanical property measurements and measurements of shrinkage. Spirobislactones were found to be effective curing agents for epoxy resins. They had greater thermal stability than the corresponding anhydride cure materials and less shrinkage occurred.

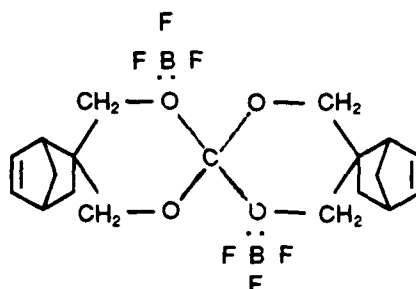
For the work reported here the epoxies were polymerized by a cationic polymerization mechanism (Bovey and Winslow, 1979).



for which HA is the polymerization initiator. HA can be any of a wide variety of materials which have active hydrogen including alcohols, aliphatic or aromatic amines, amides, or organic acids. Aromatic amine containing epoxies must be cured at a higher temperature than those cured with aliphatic amines.

An unreacted amino group of an amine curing agent can open another epoxide ring, and the OH group formed when the epoxide ring opens can open a second epoxide ring. These reactions lead to cross-linking.

DNSOC is compatible with systems reacting by cationic polymerization and therefore can copolymerize with epoxy. In order to minimize shrinkage of the epoxy, the DNSOC should not react until epoxy has reached B-stage. If polymerization of DNSOC occurs before this, the epoxy can flow in such a way as to reduce the expansion produced by polymerization of DNSOC. Polymerization of DNSOC is catalyzed by boron trichloride or boron trifluoride which lack a complete octet of electrons around the boron atom and therefore function as acid catalysts. Acid catalysis occurs when the boron compound binds to the ring oxygen atoms, permitting rupture of the O-CH₂ bond.



The objective of the program at DTRC is to reexamine the effects expanding monomers have on the mechanical properties of epoxy composites.

EXPERIMENTAL

MATERIALS

Epoxy.

1. Epon 813 (Shell Chemical Co.), diglycidyl ether of bisphenol A containing the reactive diluent cresyl glycidyl ether.
2. Epon 815 (Shell Chemical Co.), diglycidyl ether of bisphenol A containing the reactive diluents N-butylglycidyl ether and epichlorohydrin.

Curing agents.

1. XU-HY-264 (Ciba Geigy), a resinous curative product made from a phenol-formaldehyde condensate with methylene dianiline.
2. m-Phenylene diamine, (Fluka, AG, Switzerland, 99% purity).

DNSOC catalysts

3. DY9577 (Ciba Geigy), a BCl₃.amine containing catalyst.
4. Boron trifluoride - ethyl etherate (Fluka, AG, Switzerland, 48% BF₃).
5. Diethylenetriamine (Fluka, AG, Switzerland, 97% purity).

Carbon fibers.

Carbon fibers (Amoco Performance Products, Thornel PAN based carbon fiber T-300, 12 K sized with epoxy compatible sizing). Fiber properties provided by the manufacturer include: strand moduli, for which the range is 32 to 35 Msi; strand tensile strength, 450 ksi; density, 1.72 to 1.81 g/cm³; and elongation at break, 1.3%.

METHODS

DISPERSING DNSOC IN EPOXY

A stable suspension of DNSOC in Epon 813 was produced by mixing 25% DNSOC into the epoxy and rolling the mixture on a ball mill for a week or more. After ball milling, particle size of the DNSOC was measured with a Hegman gauge or determined with a measurement reticle in a light microscope. When ball milling had been done long enough, particles were 10 micrometers or smaller. It was necessary to use a low viscosity epoxy (900 cp) in order to produce the dispersion.

SHRINKAGE OR EXPANSION MEASUREMENT

Initial density was obtained by weighing a pipet, drawing up the curing agents mixed with epoxy or epoxy-DNSOC, and reading the volume. When the mixtures had solidified, the pipets were reweighed. Densities were calculated from these weight and volume measurements.

Density after curing was obtained by weighing the samples in air and then in water. Loss of mass in water provided a measurement of sample volume, which allowed calculation of density when used with the mass in air. Details of this procedure are specified in ASTM D 792-86.

PREPARATION OF BORON TRIFLUORIDE - DIETHYLENETRIAMINE COMPLEX

Equimolar amounts, measured volumetrically, of boron trifluoride-diethyletherate and diethylenetriamine (DETA) were combined inside a dry box by adding each substance to a 20 mL vial which was then capped.

PREPARATION OF THE m-PHENYLENEDIAMINE EPOXY MIXTURES

Composition of epoxy control (sample 1):

- 10 g Epon 813 epoxy,
- 0.1350 g DETA,
- 0.542 g mPDA.

Composition of DNSOC-epoxy (sample 2)

- 5 g Epon 813 epoxy containing 25% dispersed solid DNSOC,
- 5 g Epon 813 epoxy,
- 0.2250 g DETA.BF₃,
- 0.542 g mPDA.

The epoxy and epoxy-DNSOC were weighed into plastic beakers and degassed for approximately 15 minutes at room temperature inside a vacuum desiccator at a pressure of approximately 1 inch of mercury.

The mPDA and mPDA-DETA.BF₃ were weighed into separate aluminum weighing pans and placed into a 70°C oven (to melt the mPDA) which was then evacuated for approximately 10 minutes to permit degassing. The oven was filled with nitrogen, and the epoxy and epoxy-DNSOC were thoroughly mixed with their respective curing agents without allowing the mPDA to cool. The mixtures were introduced carefully into a latex

dogbone mold by means of a Pasteur pipet, and the mold was placed inside the oven on a level shelf for curing. Treatment of the mold with mold release agent prior to fiber mounting was essential for removal of the specimens without breakage. Silicone stopcock grease applied to the mold and then wiped off as much as possible, permitted easier sample removal than a spray-on type of mold release agent. The samples with the best mechanical properties were cured at 100°C for 4 hours, 2 hours at 150°C, and 180°C for 7 hours, and the samples remained in the oven as it cooled slowly to room temperature.

EMBEDDED SINGLE FILAMENT TENSILE TEST

The embedded single filament tensile test was performed by positioning carbon fibers across the eight cavities of a mold obtained from NADC and especially made for this test. Mold cavities were 2 3/8 in. long and 3/8 in. wide at the broadened ends. The narrow center portion was 3/16 in. wide and 1/16 in. deep. Fibers were held in place in the mold with cyanoacrylate glue. Since fibers were surface treated for epoxy compatibility, they were used without additional cleaning.

After curing, the samples were removed from the mold and placed in a special rack designed to fit the travelling stage of an Olympus BH-2 light microscope [Armistead, 1989]. Polarizing filters were installed in the microscope so that one filter was above the sample and one below. The lower filter could be rotated to provide optimal viewing of the strain pattern in the specimen.

When the sample was clamped in the microscope rack, a screw with a lock nut made it possible to extend the sample until breaks could be seen in the carbon fiber. These were visible because of the strain pattern at a break position which could be seen with the crossed polarizers in place. Break lengths were measured by aligning the break end with a fixed mark in the microscope eyepiece, then reading the position with the measurement scale of the travelling stage. The crossed-polarizers are essential because they make strain patterns visible in the matrix at the site of fiber breaks which otherwise could not be seen.

TENSILE PROPERTY MEASUREMENT

Tensile modulus, ultimate elongation, and ultimate tensile strengths were measured on an Instron tensile test machine.

THERMAL ANALYSIS

Differential scanning calorimetry (DSC) was done on a DuPont 9900 thermal analyzer by George Long of the Firefighting and Survivability Branch, DTRC.

DIFFERENTIAL MECHANICAL THERMAL ANALYSIS (DMTA)

DMTA was performed on a Polymer Laboratories instrument by Tim Dapp of the Polymers and Polymer Composites Branch, DTRC.

DISCUSSION AND RESULTS

In order for the expanding monomer to control epoxy shrinkage it is necessary for the expanding monomer to be present in the initial mixture as a finely divided solid.

*Armistead, Paul, Naval Research Laboratory, personal communication (1989).

When it is, the conversion from solid to liquid during copolymerization accounts for part of the expansion which the monomer produces. The remaining expansion is caused by ring-opening. For this to have a maximum effect on epoxy shrinkage control, the epoxy must form a gel well defined before the DNSOC melting and ring-opening occur. To promote this process and prevent phase separation during cure the monomer must exist as a stable dispersion in the epoxy. Production of DNSOC particles which are 10 micrometers or less is required for dispersion stability, and ballmilling was found to be a successful method for producing this dispersion, but epoxies with viscosities of 900 cp or less are required.

It was decided to work with a diglycidyl ether of bisphenol A because this type of compound is readily available commercially at a reasonable price and has been successfully used by other investigators for expanding monomer incorporation. In addition, it produces a transparent cured sample which can be used to perform the embedded single filament tensile test for which a transparent sample is required. Since both Epon 828 (Shell) and D.E.R. 332 (DuPont) have too high a viscosity (around 13,800 cp at room temperature), Epon 813 epoxy, which contains a reactive diluent, was chosen. Epoxy dilution with a reactive substance, in this case, cresyl diglycidyl ether, rather than a solvent is required so that solvent evaporation will not produce bubbles during curing.

Samples prepared with Epon 815 epoxy and XU-HY-264 and DY9577 as curing agents were found to have a considerable number of air bubbles when examined with the electron microscope (Fig. 1). In addition these samples were not transparent as is necessary to transmit light when the embedded single filament tensile test is performed. Longer degassing times prior to cure did nothing to reduce the number of bubbles, and heating to a higher temperature failed to remove the turbidity, so other sample compositions were investigated.

Dr. Bailey suggested use of m-phenylene diamine (mPDA) as a curing agent for the epoxy with use of BF_3 as a catalyst for ring opening and copolymerization of DNSOC with the epoxy. With mPDA, epoxy cure takes place at a lower temperature than the ring opening polymerization of the DNSOC catalyzed by BF_3 .

For this work the boron trifluoride was purchased as the ether complex. However, it was discovered that this form is difficult to work with since it has high volatility and fumes vigorously in moist air because of its highly hygroscopic nature. Moreover, complexes of BF_3 and mPDA formed by addition of the etherate to mPDA in a dry box were very high melting and therefore difficult to blend with the epoxy-DNSOC dispersion. Therefore, the BF_3 .etherate was combined by pipet measurement with an equimolar quantity of DETA inside a dry box. When this mixture was stored inside a capped vial in a vacuum desiccator it remained liquid indefinitely and could be conveniently weighed and blended with the epoxy-DNSOC.

A number of methods have been used to evaluate the shrinkage which occurs during curing and its effects on stress in the cured epoxy. Dr. Piggott employed thin strips of metal which were heated in an oven to produce a cure. Measurement of the amount the strip deviates from linearity provides a measure of the epoxy shrinkage stress on the surface it contacts. The advantage of this method is that it provides a measure of stress which the epoxy exerts on the strip following curing, and measurement of volume shrinkage alone does not do this. This method was not pursued at DTRC in part because of difficulty in producing a uniform epoxy coating on the strip.

For this work, shrinkages of epoxy and DNSOC-epoxy during curing were obtained by measurement of density before and after cure. This method provided satisfactory accuracy. Volume after cure could not be obtained with the volumetric pipet used to obtain density before cure because cure shrinkage caused meniscus distortion, and in addition, the epoxy pulled away from the interior wall of the pipet. Therefore, density measurements were obtained by water displacement as specified in ASTM D 792-86 and used to evaluate sample shrinkage or expansion.

Very large shrinkage reduction was achieved with the DNSOC-epoxy cured with mPDA and BF₃.DETA (sample 2, more than 5%) as can be seen in Table 1. This shrinkage reduction is much larger than that reported by Shimbo et al (1985) who found 2.8% shrinkage in the glassy region of the epoxy when 25% expanding monomer was used. In addition, their system phase separates into a glassy and a rubbery region, whereas no phase separation is seen in our system.

Mechanical properties of epoxy and DNSOC-epoxy cured with mPDA and BF₃.DETA (samples 1 and 2) are shown in Table 2. From this table it is seen that tensile strength is reduced by approximately 40% when 11.7% DNSOC is incorporated into epoxy, and the tensile modulus is unchanged.

Table 1. Volume effect of incorporating DNSOC.*

Substance	Curing Agents	Highest Cure Temp °C	Volume Change
Epoxy (Epon 815)	Ciba-Geigy HY-XU-264	100	3.3% shrinkage
Epoxy-DNSOC (13%)	Ciba-Geigy HY-XU-264	100	4.7% expansion
Epoxy (Epon 813)	mPDA DETA	180	5.4% shrinkage
Epoxy-DNSOC (11.7%)	mPDA BF ₃ .DETA	180	0% shrinkage

*For full names of substances see text.

Table 2. Tensile properties.

Substance	Curing Agent	Cure Temp °C	Tensile Modulus (ksi)	Elongation at Break (%)	Tensile Strength (psi)
Epoxy (Epon 813)	mPDA*	180	200(4)±40	5.0	6600(4)±700
DNSOC-epoxy (11.7%)	mPDA	180	230(3)±50	4.2	3700(2)±100

*m-phenylenediamine.

The embedded single filament tensile test was performed by mounting a special rack on the travelling stage of a light microscope fitted with crossed polarizers. For the

epoxy sample cured at 180°C and allowed to cool slowly in the oven, no strain pattern was seen in the epoxy matrix before application of a tensile stress. For the sample cured at a maximum temperature of 150°C, there was a very pronounced strain pattern which produced red and green coloration when viewed through the crossed polarizers. For this sample also there was a noticeable waviness in the carbon fiber, indicating that the epoxy was exerting a compressive stress on the fiber. Low compressive impact strength would be expected from a sample with these characteristics.

Examination of epoxy samples under the microscope with polarizers in place revealed that some stress in cured epoxy is related to the fact that epoxy contracts longitudinally along carbon fibers causing them to bend slightly. Because these fibers are very stiff, a strain is produced in the epoxy matrix which appears as colored areas when seen under the microscope. Colored areas were seen in the epoxy matrix even at considerable distances from the fibers, indicating that there are also stresses in the matrix which are not caused by the fiber. These probably develop during cooling. On samples which are heated for a longer time, and which were allowed to cool down slowly, no stress patterns were seen in the epoxy in the absence of a tensile force.

The characteristic length, l_c , obtained from the embedded single filament tensile test, was calculated by use of Weibull analysis. Results with the epoxy samples are shown in Fig. 2. Most probable values for l_c were found to be 0.79 and 0.98 mm for the DETA (sample 1) containing samples cured at 180°C. When this value is substituted into the relation $\tau_c = \sigma_c d / 2l_c$, the value found for τ_c , the interfacial tensile stress is 19.7 MPa (2862 psi) when σ_c , the fiber tensile strength is taken to be 450 ksi. This value is close to the interfacial pressure value, 20 MPa, found by Dr. Piggott for carbon fiber reinforced DGEBA.

A sample which contained 10 g of Epon 813 epoxy and 1.5 g mPDA cured at 150°C gave a limiting fragment size of 1.03 mm and τ_c equal to 17.0 MPa (2473 psi).

When the embedded single filament tensile test was performed on DNSOC-epoxy samples, the fibers slipped as the specimen was extended, so that a small number of fiber breaks allowed the tensile stress to be relieved. Because this sample did not show a strain pattern at the fiber breaks, breaks could not readily be found with the microscope. Therefore, the matrix was dissolved by heating the sample in concentrated nitric acid overnight on a steam bath, and the fiber fragments were collected on a fritted glass filter. The lengths were determined by direct examination with a low power microscope and were found to be 1 to 2 cm in length. These values cannot be used to make a valid calculation of interfacial tensile stress because they indicate that the fiber was slipping in the matrix. However, if 1 cm is taken to be the value for l_c , the interfacial tensile stress has, very approximately, the value 1.8 MPa. This value is significantly smaller than the value found for epoxy and is far below optimal. Therefore, it appears that much smaller amounts of DNSOC can be used to reduce strain produced by shrinkage on the fibers.

Thermal analyses of several different epoxy and DNSOC-epoxy compositions were run. These results appear in Figs. 3 and 4. Figure 3a shows a DSC plot of the epoxy, Fig. 3b shows a scan of the DNSOC only, and 3c is a plot of a DNSOC-epoxy sample cured with XU-HY-264 and DY9577. The minimum at 240°C, in Fig. 3b is produced by the melting of DNSOC. When this plot is compared with the DSC results in Fig. 3c, it is apparent that there is little indication of the DNSOC melting point remaining in the

DNSOC-epoxy mixture after curing, indicating that nearly all of the DNSOC is copolymerized with the epoxy.

For the DNSOC-epoxy cured with mPDA and $\text{BF}_3\cdot\text{DETA}$ (Fig. 4a), the DNSOC has apparently once again almost entirely copolymerized with the epoxy because there is little indication of a DNSOC melting point at 240°C . Longer curing (Fig 4b) results in a lower intensity for the peak at 280°C and an increase in the height of the peak at 360°C , suggesting development of increased thermal stability during heating.

DMTA results are shown in Fig. 5. E' , the tensile storage modulus, and E'' , the tensile loss modulus, are shown for sample 1 in Fig. 5a. $\tan \delta (= E''/E')$ for these data are in Fig. 5b. For the DNSOC-epoxy (sample 2) E' and E'' appear in Fig. 5c and $\tan \delta$ is plotted in Fig. 5d. Maxima in $\tan \delta$ give values for T_g of 100°C for the epoxy and 90°C for the DNSOC-epoxy. This T_g lowering is in agreement with the T_g lowering reported by Shimbo et al for a similar percentage of DNSOC in epoxy. However, much larger shrinkage reductions were observed by us with this quantity of DNSOC than were reported by Shimbo.

This work, which builds upon that of others, confirms that it is necessary to carefully control the time during cure at which the ring opening occurs if one is to minimize shrinkage. The epoxy must first begin to gel so that a certain rigidity is built in before the expanding monomer copolymerizes. Both Shimbo et al (1985) and Ishida et al (1988) attribute changes in mechanical properties to lowering of T_g . The investigations conducted by Shimbo differ from those described here in that the expanding monomer was a spiro orthoester (rather than DNSOC) and it was attached directly to the glycidyl ether portion of bisphenol A. Their catalyst system also differed from the one reported here. Phase separation into rubbery and crystalline regions was reported, and the ring opening occurred during the curing process, rather than after gelation of the epoxy. In addition, the phase change occurring when solid DNSOC dissolves in the epoxy did not occur in their system. The result is that 25% of expanding monomer reduced shrinkage by only 0.9% as compared with the shrinkage reduction of approximately 5% seen by us with 11.7% DNSOC. Ishida and Nigro (1988) employed Epon 828 (a diglycidyl ether of bisphenol A) but used a single catalyst (BF_3) so that once again ring opening occurred during curing. For both these experimental situations the beneficial effects of ring opening were therefore not fully realized.

CONCLUSIONS

Incorporation of 11.7% DNSOC into the epoxy eliminated sample shrinkage and caused a very large reduction of interfacial tensile stress, as shown by the approximate tenfold increase in fiber fragment length obtained for DNSOC-containing samples. Longitudinal stresses on the fiber, which produced pronounced waviness in the cured specimen, were also greatly reduced, as evidenced by the absence of waviness in the DNSOC-containing samples. Furthermore, matrices containing the DNSOC did not show the colored strain pattern seen with identically cured epoxy, indicating that DNSOC reduces strain in the matrix as well as near the fibers. For formulations used in this research, reductions in T_g are modest (10°C) and therefore do not appear to be the primary cause of stress reduction in the DNSOC-epoxy as reported by Shimbo et al.

In this work, a formulation was found which allowed performance of the embedded single filament tensile test, and, from these results it is apparent that a much larger amount (11.7%) of DNSOC was employed than is necessary to produce optimal epoxy matrix shrinkage. More research needs to be done to find the optimal level. To be useful for engineering applications, a higher performance type of epoxy should be tested.



Fig. 1. Epon 815 epoxy cured with HY-XU-264 showing trapped bubbles.

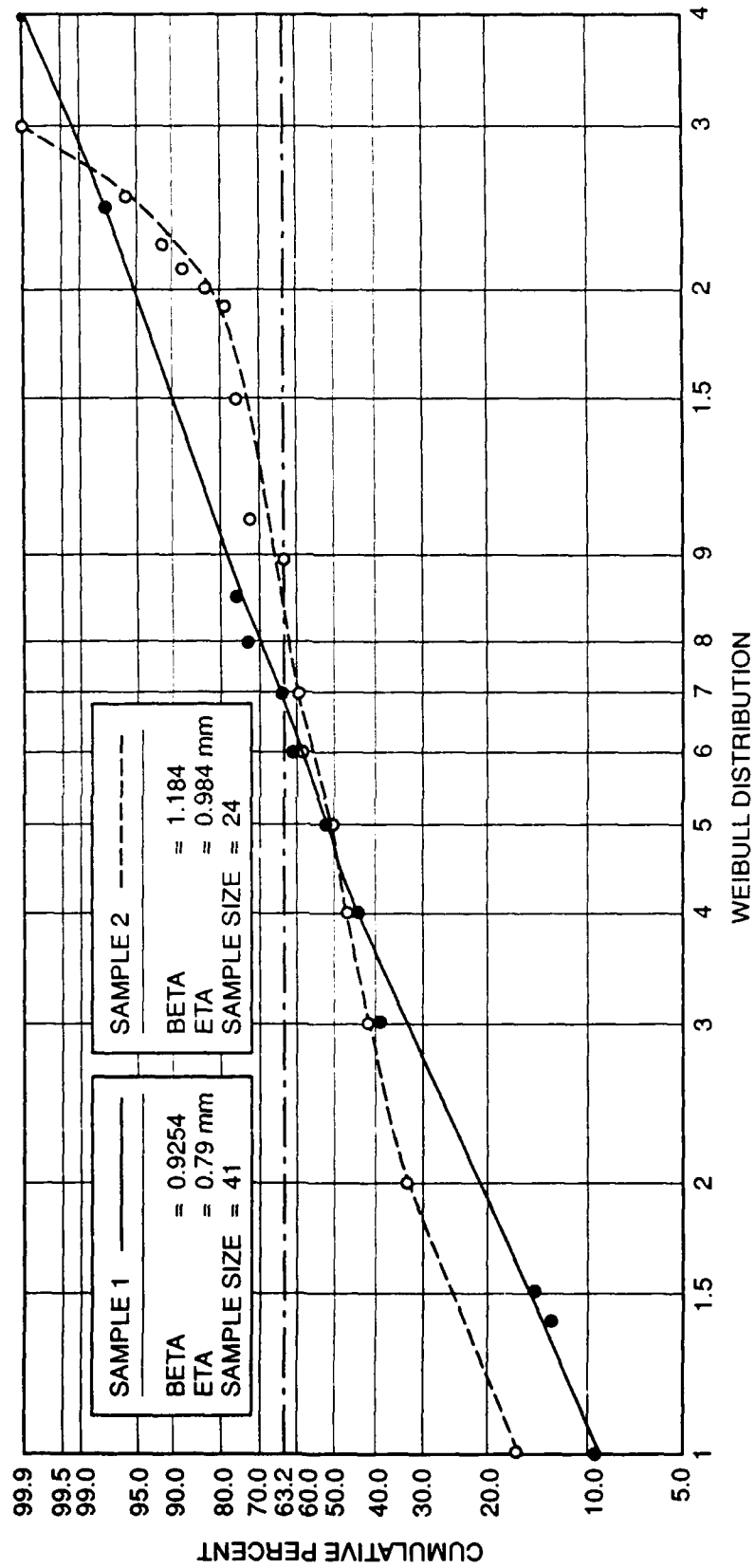


Fig. 2. Weibull distribution plots of Epon 813 epoxy samples for which l_c values were found to be 0.79, 0.98 and 1.03 mm.

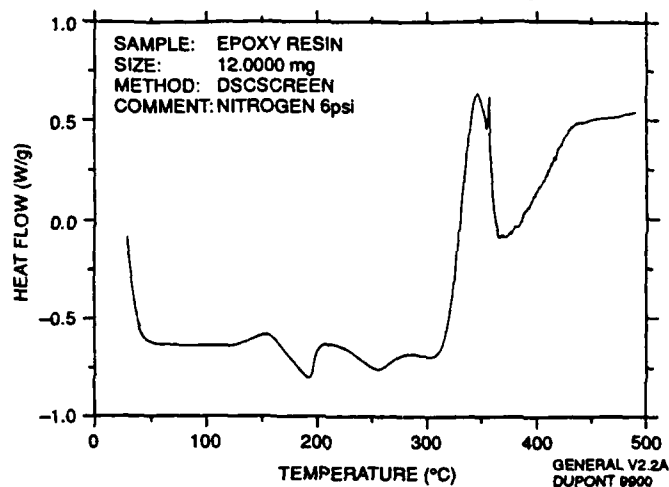


Fig. 3a.

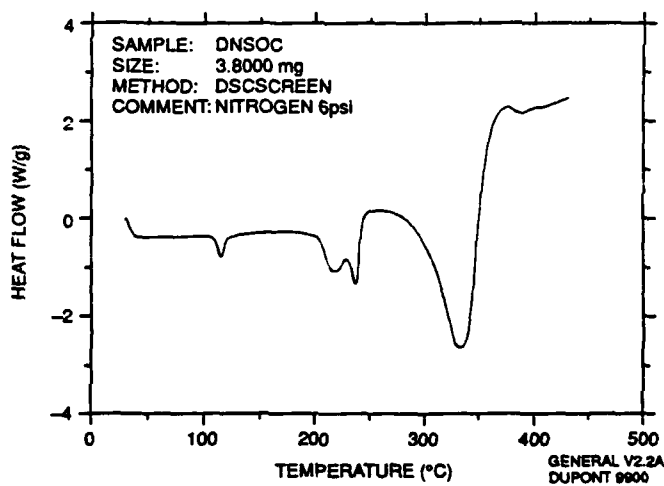


Fig. 3b.

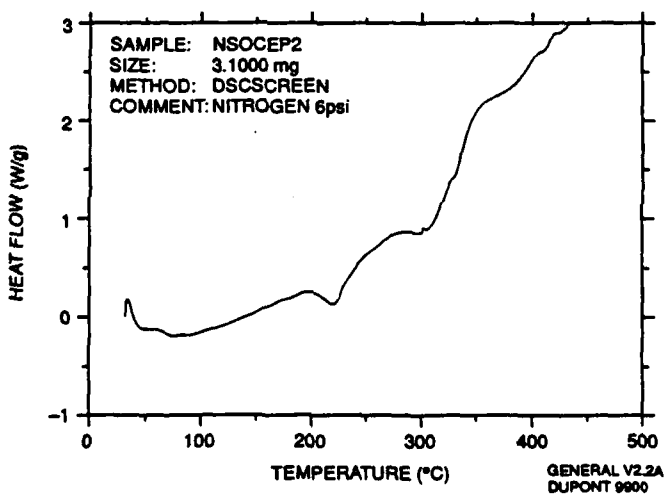


Fig. 3c.

Fig. 3. Differential scanning calorimetry (DSC) scans of (a) epoxy (Epon 815);
 (b) DNSOC; and (c) DNSOC-epoxy showing loss of melting point indication
 at 240° for the DNSOC epoxy.

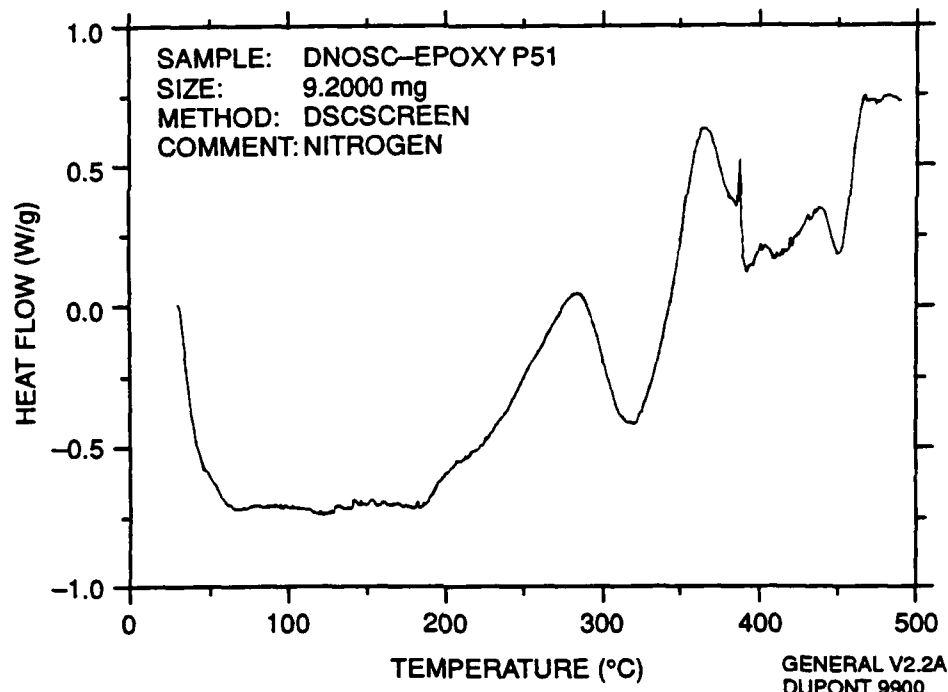


Fig. 4a.

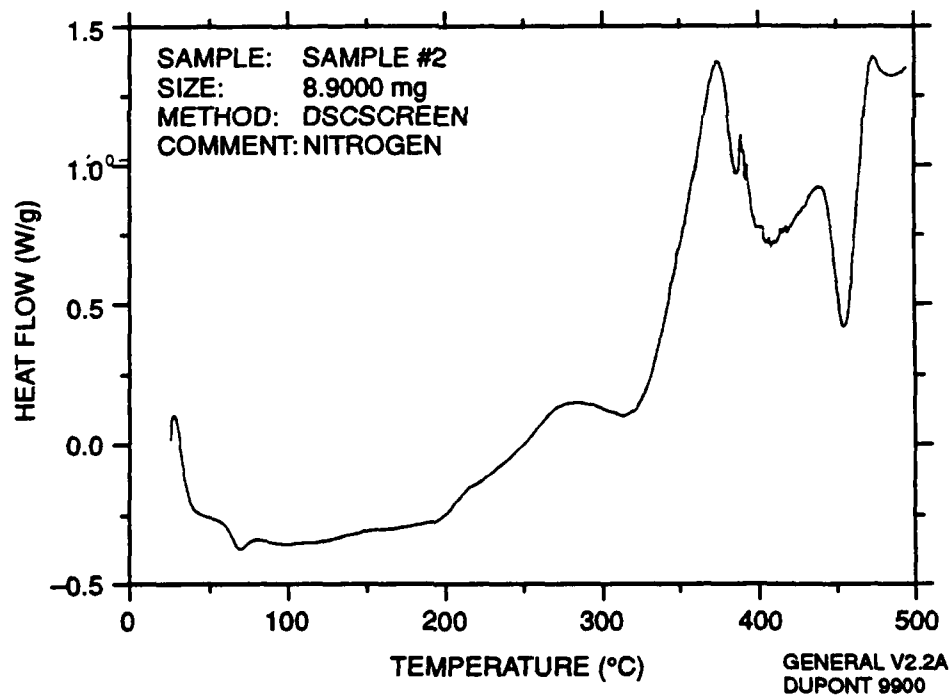


Fig. 4b.

Fig. 4. DSC scans of DNSOC-epoxy (Epon 813) after heating: (a) 75 min at 150°C; and (b) 24 hours at 150°C.

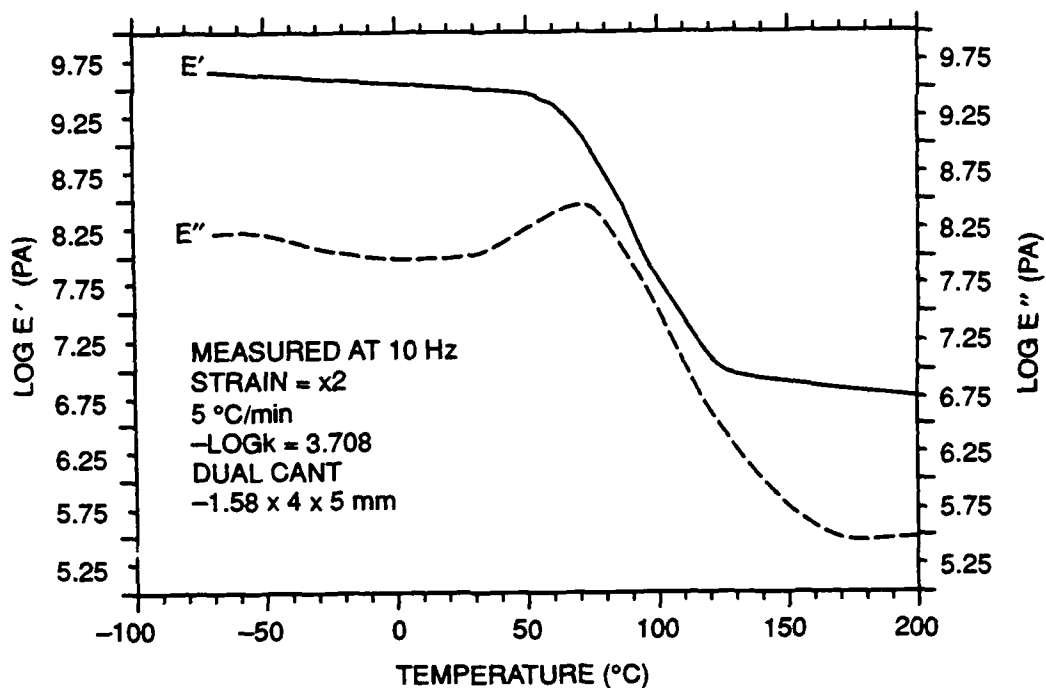


Fig. 5a.

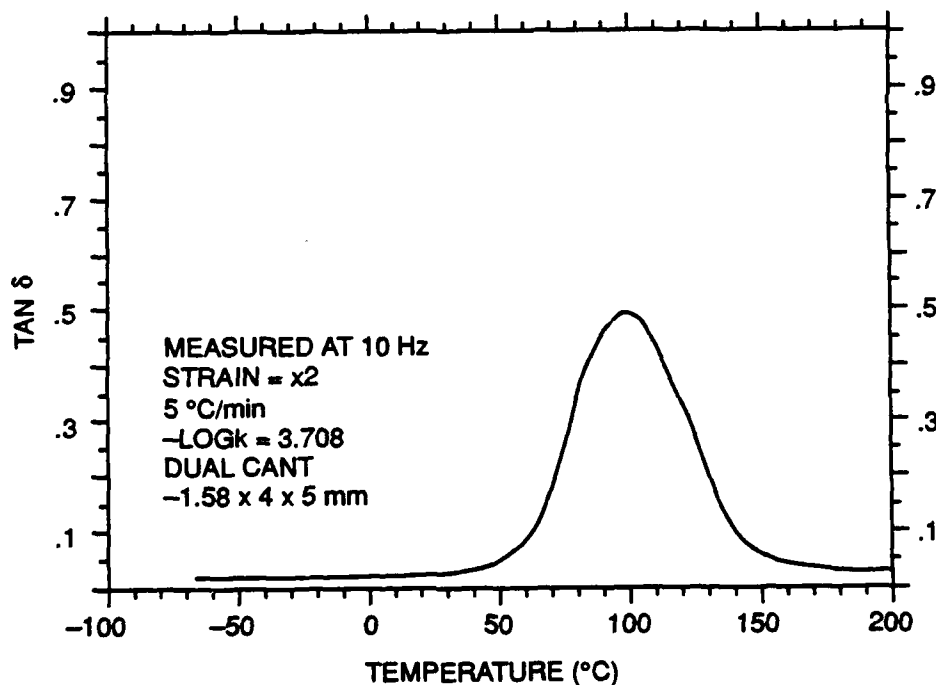


Fig. 5b.

Fig. 5. DMTA for epoxy (sample 1): (a) E' and E'' as a function of temperature; and (b) $\tan \delta$ values.

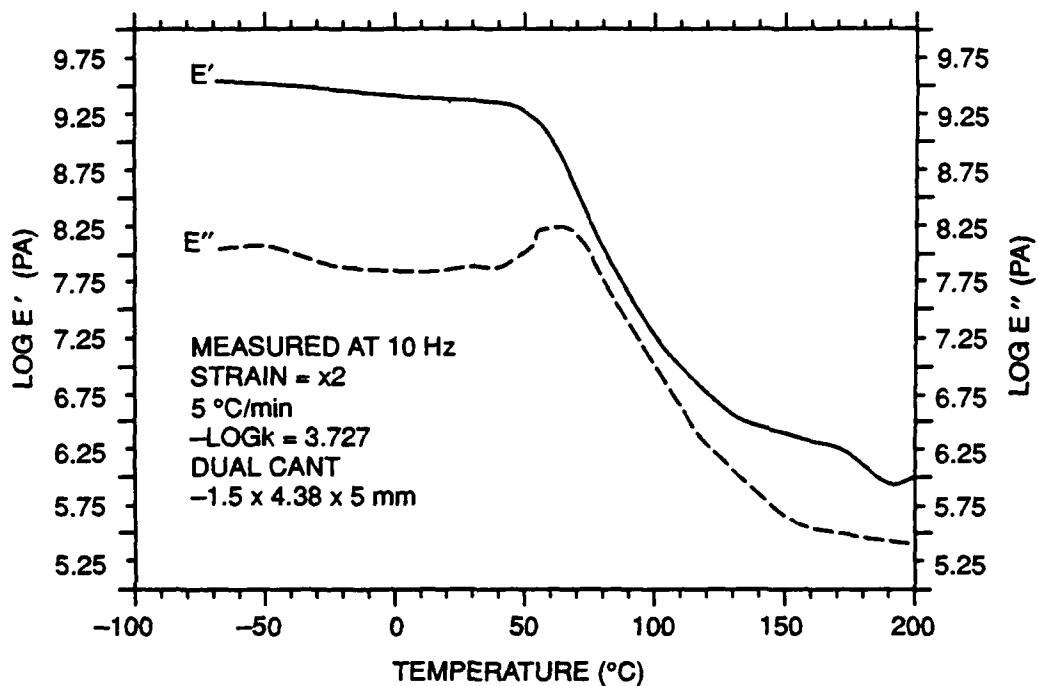


Fig. 5c.

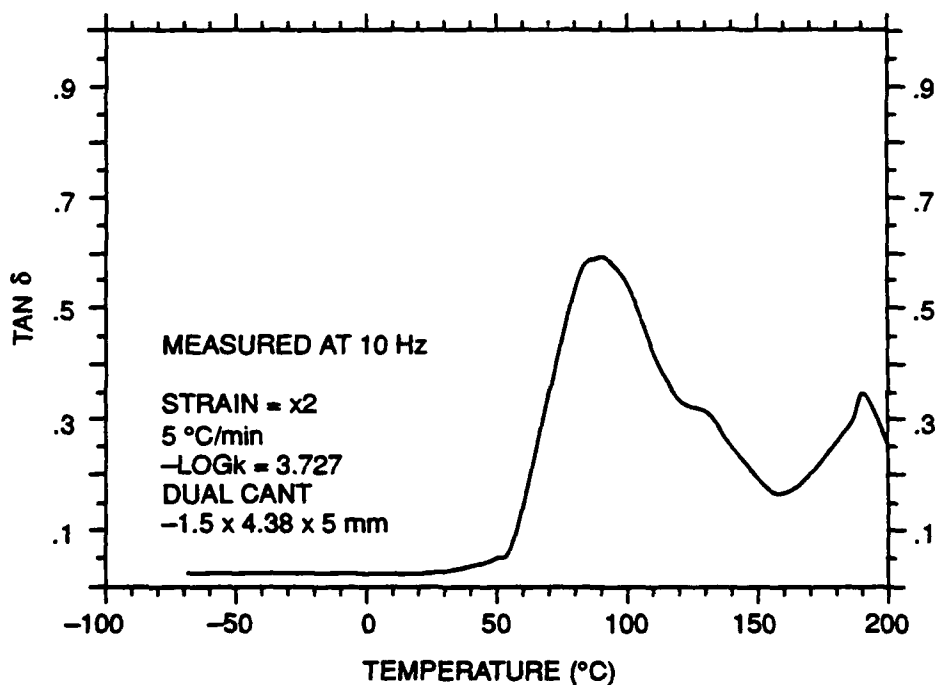


Fig. 5d.

Fig. 5. (continued) DTMA for DNSOC-epoxy (sample 2): (c) E' and E'' as a function of temperature; and (d) $\tan \delta$ values.

REFERENCES

- Bailey, W.J., P.L. Sun, H. Katsuki, T. Endo, H. Iwama, R. Tsushima, K. Saigo, M. M. Bittrito, "Ring-Opening Polymerization," T. Saegusa and E. Goethals, Eds., ACS Symposium Series, No. 59, p. 38 (1977).
- Bovey, F.A. and J.H. Winslow, *Macromolecules, An Introduction to Polymer Science*, Academic Press, New York, p. 160 (1979).
- Ishida, H. and J. Nigro, *Polymeric Materials Science and Engineering*, Vol. 59, pp. 859-862 (1988).
- Piggott, M.R., P.W.K. Lam, J.T. Lim, and M. S. Woo, *Composites Science and Technology*, Vol. 23, pp. 247- 262 (1985).
- Piggott, M.R., Sixth International Conference on Composite Materials and 2d European Conference on Composite Materials, F.L. Matthews, N.C.R. Buskell, J.M. Hodgkinson, and J. Morton, Eds., Vol. 4, London, pp. 180-189 (July 20-24, 1987).
- Shimbo, M., M. Ochi, T. Inamura, and M. Inoue, *J. of Materials Science*, Vol. 20, pp. 2965- 2972 (1985).
- Sikes, A.M., and R.F. Brady, "Controlled Shrinkage Polymers: Characterization of Epoxy Resins Cured With Spirobis lactones," NRL report (19 Oct 1989).

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